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(54) PIGMENTED POLYAMIDES

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
This invention relates to the pigmentation of polyamides and more particularly to the pigmentation of copolymers of hexamethylenediammonium adipate and caprolactam.
It is known that the incorporation of pigments, in particular organic pigments, into polyhexamethylene adipamide markedly reduces the stability of the polyamide to heat treatments, resulting in the formation of gels in much shorter time. This is of considerable disadvantage when the pigmented polyamides are subsequently to be melted and spun into fibres since the short gel times of the pigmented polyamides (i.e. the times for which the polyamides can be subjected to heat without the formation of gels) and result in difficulties in the production of fibres of satisfactory physical properties. It has been found that this disadvantage can be overcome by using a polymer from hexamethylenediammonium adipate containing up to 10% by weight of caprolactam whereby the gel times of the pigmented polymers are approximately the same as those of the uncoloured polyhexamethylene adipamide polymers.
According to the invention there is provided a process for the preparation of pigmented polyamides which comprises polymerising a mixture of from 90 to 99.5% by weight of hexamethylenediammonium adipate and from 0.5 to 10% by weight of caprolactam in the presence of an organic pigment.
The process of the invention can be conveniently carried out under the conditions normally employed for polymerising hexa-

methylenediammonium adipate. Thus, for example, the caprolactam and the finely divided pigment can be added to an aqueous solution of the hexamethylenediammonium adipate, and the resulting mixture heated in an autoclave to a temperature in the region of 275°C. while the water, in the form of steam, is allowed to slowly escape from the autoclave.
If desired a viscosity stabiliser such as acetic acid can also be added to the reaction mixture. Also, if desired, there can be used a mixture of equimolecular proportions of hexamethylenediamine and adipic acid instead of the hexamethylenediammonium adipate, and ε-aminocaproic acid in place of the caprolactam.
At the conclusion of the process the pigmented polyamide is discharged from the autoclave and converted into chip form, which can subsequently be melted and spun into fibres.
It is preferred that the finely divided pigment be used in the form of an aqueous dispersion of the pigment, which dispersion preferably contains a dispersing agent, which may be cationic, anionic or non-ionic. The pigments are used in finely divided form, that is to say in a form such that over 95% of the material comprises particles of less than 3 microns in size. If desired mixtures of two or more pigments can be used. As specific examples of organic pigments which can be used in the process of the invention there may be mentioned quinacridone pigments, phthalocyanine pigments such as copper phthalocyanine, and perylene pigments such as the bis - N:N'(3:5'-dimethylphenyl)imide of perylene - 3:4:9:10-tetracarboxylic acid. If desired inorganic pigments, such as titanium dioxide, carbon black, cadmium sulphide, cadmium selenide and iron oxide, can be used in conjunction with the organic pigment.
The invention is illustrated but not limited 90

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by the following Examples in which the parts and percentages are by weight.

EXAMPLE 1

- 996 parts of hexamethylenediammonium adipate, 45 parts of caprolactam, 600 parts of water, 1.43 parts of acetic acid and 38.1 parts of aqueous dispersion containing 23.6% of copper phthalocyanine and 1.8% of the disodium salt of bis(1 - sulphonaphth-2 - yl) methane are charged to an autoclave. The autoclave is heated to 100°C., purged with steam and then sealed. The autoclave is then heated to a temperature of 215°C., while the pressure rises to 250 lbs./sq. in. (p.s.i.). This pressure is maintained by slow release of steam while the temperature is raised to 235°C. The pressure is then reduced during 1 hour to atmospheric pressure whilst the temperature is raised to 275°C. The reaction mixture is finally maintained at this temperature for 20 minutes. The molten polyamide is then discharged from the autoclave under nitrogen pressure.

When the resulting polyamide is subsequently heated at 300°C. in an atmosphere of steam, the viscosity of the polyamide reaches 10000 poises as a result of gel formation after 20 hours heating, compared with 7 hours for a polyamide prepared as described above except that the 45 parts of caprolactam were omitted from the autoclave.

The following Table gives further Examples which illustrate the process of the invention, which were carried out in similar manner to that described in Example 1. In this Table Column 2 lists the amount of hexamethylene diammonium adipate used, Column 3 the amount of caprolactam, Column 4 the amount of water, Column 5 the amount of acetic acid, Column 6 the pigment and the dispersing agents and the amounts thereof which were used, and

Column 7 gives the gel time for the resulting polyamide.

*Hexamethylene
diammonium
adipate*

<i>Example</i>	<i>Caprolactam</i>	<i>Water</i>	<i>Acetic acid</i>	<i>Pigment and dispersing agent</i>	<i>Gel time</i>
2	1017 parts	600 parts	1.43 parts	9 parts copper phthalocyanine 0.7 part of disodium salt of bis(1 - sul- phonaphth - 2 - yl)methane	22 hours
3	1038 parts	600 parts	1.43 parts	9 parts of copper phthalocyanine 0.7 part of disodium salt of bis(1 - sul- phonaphth - 2 - yl)methane	15½ hours
4	996 parts	780 parts	1.43 parts	14.5 parts of bis(methylimide) of peryl- ene 3:4:9:10 - tetracarboxylic acid 1.6 parts of disodium salt of bis(1 - sul- phonaphth - 2 - yl)methane	14½ hours
5	1017 parts	780 parts	1.43 parts	14.5 parts of bis(methylimide) of peryl- ene 3:4:9:10 - tetracarboxylic acid 1.6 parts of disodium salt of bis(1 - sul- phonaphth - 2 - yl)methane	12½ hours
6	234 parts	140 parts	0.27 part	1.04 parts of copper phthalocyanine 0.1 part of disodium salt of bis(1 - sul- phonaphth - 2 - yl)methane	22½ hours
7	234 parts	140 parts	0.27 part	1.06 parts of copper phthalocyanine 1.14 parts of the bis-benzimidazole of perylene 3:4:9:10 - tetracarboxylic acid 0.15 part of carbon black 2.35 parts of disodium salt of bis(1 - sul- phonaphth - 2 - yl)methane	17½ hours

The gel time for the coloured polyamides prepared entirely from hexamethylenediammonium adipate corresponding to Examples 5, 6 and 7 were $10\frac{1}{2}$ hours, $20\frac{1}{2}$ hours and $15\frac{1}{2}$ hours respectively.

WHAT WE CLAIM IS:—

1. Process for the preparation of pigmented polyamides which comprises polymerising a mixture of from 90 to 99.5% by weight of hexamethylenediammonium adipate and from 0.5 to 10% by weight of caprolactam in the presence of an organic pigment.
2. Process as claimed in Claim 1 wherein the pigment is used in the form of an aqueous dispersion.
3. Process as claimed in Claims 1 or 2 wherein the pigment is a copper phthalocyanine pigment.

4. Process as claimed in any of Claims 1 to 3 wherein there is used a mixture of pigments.

5. Process as claimed in any of Claims 1 to 4 wherein there is additionally used an inorganic pigment.

6. Process as claimed in any of Claims 1 to 5 wherein the polymerisation is carried out in the presence of a viscosity stabiliser.

7. Process for the preparation of pigmented polyamides as claimed in any of Claims 1 to 6 as hereinbefore particularly described especially with reference to any of the Examples.

8. Polyamides which have been pigmented by a process as claimed in any of Claims 1 to 7.

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